



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03291691.8

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



**Europäisches
Patentamt**

**European
Patent Office**

**Office européen
des brevets**

Bescheinigung

Certificate

Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

03291691.8

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
p.o.

R C van Dijk



Anmeldung Nr:
Application no.: 03291691.8
Demande no:

Anmeldetag:
Date of filing: 08.07.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
2596 HR Den Haag
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se référer à la description.)

Process to prepare a base oil

In Anspruch genommene Priorität(en) / Priority(ies) claimed /Priorité(s)
revendiquée(s)

Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

C10G/

Am Anmeldetag benannte Vertragsstaaten/Contracting states designated at date of
filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT RO SE SI SK TR LI

**CERTIFIED COPY OF
PRIORITY DOCUMENT**

PROCESS TO PREPARE A BASE OIL

Field of the Invention

The invention relates to a process to prepare a lubricating base oil having a saturates content of more than 90 wt%, a sulphur content of less than 0.03 wt% and a viscosity index (VI) of more than 80.

Background of the Invention

Such a base oil is sometimes referred to as an API Group II base oil when the VI is between 80-120 or an API Group III base oil when the VI is higher than 120. It is defined in API Publication 1509: Engine Oil Licensing and Certification System, "Appendix E-API Base Oil Inter-changeability Guidelines for Passenger Car Motor Oil and Diesel Engine Oils". There exist an increasing demand for these products due to the fact that modern automobile engines operate under more severe conditions, requiring a lubricating oil which is formulated based on a base oil having the above specifications. The API Group II and III base oils are also valuable for Industrial Lubricants, because of their improved inhibited oxidation stability.

Lubricating base oils are conventionally prepared starting from a vacuum distillate or a deasphalted vacuum residue. These distillates are obtained by first distilling a petroleum crude feedstock at atmospheric conditions wherein a residue is obtained, which residue is subsequently distilled at reduced pressure obtaining vacuum distillates and a vacuum residue. Aromatics are removed from the vacuum distillate by means of solvent extraction resulting in an aromatic-poor solvent extracted product. In a subsequent step wax is removed from the solvent extracted product and an intermediate

lubricating base oil product is obtained. Typically the wax is removed by solvent dewaxing. The product obtained by such a process is referred to as 'Solvex' base oil. It has been found that the API Group II and III base oil product cannot be easily obtained by such a process from most petroleum crude sources. An overview of typical routes to API Group I, II and III base oils is for example described in Oil & Gas Journal, Sept. 1, 1997, pages 63-70.

To increase the VI and the amount of saturates of a base oil product a hydroprocessing step can be used. Conventional hydroprocessing catalysts are generally in the form of a carrier of a refractory oxide material on which hydroprocessing metals are deposited, the choice and amount of each component being determined by the end use. Refractory oxide materials usual in the art are amorphous or crystalline forms of alumina, silica and combinations thereof. These oxide materials can have some intrinsic activity but often only provide the support on which active metal compounds are held. The metals are generally combinations of non-noble metals from Group VIII and Group VIb of the Periodic Table which are deposited in oxidic form during manufacture. Optionally, the oxides are then sulphided prior to use to enhance their activity.

WO-A-0073402 describes a process to prepare an API Group II base oil starting from a solvex base oil by first contacting the solvex base oil with a NiMo on alumina catalyst, then separating off a sulphur containing gas fraction and subsequently contacting the liquid effluent with a Pt/Pd on silica-alumina catalyst. A disadvantage is the complexity of such a multistep process. The object of the present invention is to provide a simpler process.

Summary of the invention

This object is achieved by the following process. Process to prepare a lubricating base oil having a saturate content of more than 90 wt%, a sulphur content of less than 0.03 wt% and a viscosity index of more than 80 starting from an intermediate lubricating base oil product having a saturates content of below 90 wt% and a sulphur content of above 0.03, which intermediate lubricating base oil product is obtained by first removing part of the aromatic compounds by means of solvent extraction of a petroleum fraction boiling in the lubricating base oil range resulting in a solvent extracted product and subsequently solvent dewaxing the solvent extracted product to obtain the intermediate lubricating base oil product wherein said intermediate product is contacted with a hydroprocessing catalyst in the presence of hydrogen, wherein said hydroprocessing catalyst comprises one or more metals of Group VIII and one or more metals of Group VIb in their oxide or sulfide form and the total content of the metals, calculated as if they are in their oxidic form, is greater than 60 wt%.

Brief description of drawings

Figure 1 shows the amount of saturates in weight percentage as a function of the reaction temperature in degrees Celsius for the base oils obtained in the Experiments.

In Figure 2 the VI as function of the reaction temperature is depicted for the catalysts used in the Experiments.

Detailed description of the invention

Applicants have found that an API Group II or Group III base oil can be prepared by a simpler process starting from a solvex base oil when using the process

according to the present invention. An additional ,
advantage is that the desired product can be made using
widely available feedstock, namely base oils obtained by
solvent extraction and solvent dewaxing. These base oils
do not necessarily have to be prepared at the same
location as where the process according the invention
takes place. This is advantageous when existing
hydroprocessing facilities to prepare base oils are not
at the same location as the solvent extraction and
dewaxing facilities.

For this invention the sulphur and nitrogen content
expressed in weight percentage or ppmw is the amount of
elemental sulphur or nitrogen relative to the total
amount of the mixture referred to.

The intermediate lubricating base oil product having
a saturates content of below 90 wt% is obtained by
solvent extraction and dewaxing of a petroleum fraction
boiling in the lubricating oil range. Suitable distillate
petroleum fractions are vacuum distillate fractions
derived from an atmospheric residue, i.e. distillate
fractions obtained by vacuum distillation of a residual
fraction which in return is obtained by atmospheric
distillation of a crude oil. The boiling range of such a
vacuum distillate fraction is usually between 300 and
620 °C, suitably between 350 and 580 °C. However,
deasphalted residual oil fractions, including both
deasphalted atmospheric residues and deasphalted vacuum
residues, may also be applied.

Solvent extraction is a widely applied technology
when preparing base oils and is for example described in
"Lubricating base oil and wax processing", by Avilino
Sequeira, Jr., 1994, Marcel Dekker Inc. New York,
pages 81-118. Solvent extraction is suitably performed
with for example N-methyl-2-pyrrolidone, furfural, phenol
and sulphur dioxide as extraction solvent. Often used

solvents are N-methyl-2-pyrrolidone and furfural. In the solvent extraction aromatic compounds are partly removed from the hydrocarbon mixture, thereby increasing the viscosity index of the product. Amounts of sulphur and nitrogen are also removed in the solvent extraction process.

Solvent dewaxing is a widely applied technology when preparing base oils. Possible solvent dewaxing processes are described in the earlier mentioned textbook "Lubricating base oil and wax processing", by Avilino Sequeira, Jr., 1994, Marcel Dekker Inc. New York, pages 153-192. Solvent dewaxing is performed by chilling the feedstock with a solvent whereby the wax molecules crystallise. The wax crystals are subsequently removed by filtration and the solvent is recovered. Examples of possible solvents are methylethylketone/toluene, methylisobutylketone, methylisobutylketone/methylethylketone, dichloroethylene/methylenechloride, and propane.

The intermediate lubricating base oil product as obtained by solvent extraction and solvent dewaxing contains less than 90 wt% saturates and has a sulphur content higher than 300 ppmw. It has been found that the intermediate base oil product may contain high amounts of sulphur, for example more than 1000 ppmw and up to 3 wt%. Such sulphur levels do not adversely affect the catalyst activity. This is advantageous because a greater range of solvex base oils may be used as base oil intermediate product in the present invention. The nitrogen content is preferably less than 50 ppmw. The saturates content is preferably higher than 70 wt%. Next to saturates the base oil mainly consists of aromatic and polar compounds. Examples of polar compounds are specific sulphur and nitrogen containing compounds. The pour point is usually less than 0 °C, more preferably less than -15°C. Particularly suitable base oils to be used in the present

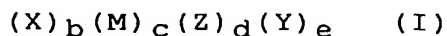
invention are those which are classified as API Group I Base Oils as described in the afore-mentioned API Publication 1509: Engine Oil Licensing and Certification System, "Appendix E-API Base Oil Interchangeability Guidelines for Passenger Car Motor Oil and Diesel Engine Oils".

In the process according to this invention the level of sulphur and nitrogen is reduced, the amount of saturates is increased and the viscosity index is improved. Suitable catalysts for the process according to this invention comprise at least one Group VIb metal component and at least one Group VIII metal component. The Group VIb metal component used is preferably molybdenum (Mo), tungsten (W) or chromium (Cr), more preferably Mo or W. Chromium is preferably not used because of environmental reasons. The Group VIII metal used is preferably a non-noble group VIII metal, more preferably nickel (Ni) and/or cobalt (Co). Suitable metal combinations are one or more Group VIII and one or more Group VIb metal, preferably one Group VIII metal and one or more Group VIb metal, more preferably one Group VIII metal and one Group VIb metal. Examples of suitable catalysts include those catalysts comprising the following combinations of Group VIII and Group VIb metals: NiW, NiMo, NiMnMo, CrNiMo, CoMoW and NiMoW. The total amount of Group VIb metal and Group VIII metal is greater than 60 percent by weight (wt%), preferably greater than 75 wt%, calculated as if the metals are in their oxidic form, relative to total weight of catalyst. Although the metals may be present in other forms, i.e. elemental and/or sulphides, it is presumed for the weight fraction calculations that all metals present are in their oxidic form.

Preferably also a refractory oxide is present. The refractory oxide may be any inorganic oxide, optionally

in combination with an inert binder material. Examples of suitable refractory oxides include inorganic oxides, such as silica, alumina, magnesia, titania, zirconia, boria, zinc oxide, natural and synthetic clays, and mixtures of two or more of these. Preferred materials are silica, alumina and titania, and mixtures thereof and/or with small amounts of zinc oxide. Most preferred is silica. The amount of refractory oxide is suitably in the range of from 5, preferably from 10, more preferably from 15, to 40 wt%, preferably to 30, more preferably to 25, especially to 20. Preferred compositions contain from 10 to 30 wt%, more preferably from 15 to 25 wt%. Catalyst containing such a high amount of metals and a limited amount of inert refractory oxide are called 'bulk metal oxide catalysts'. Group VIb and Group VIII refers to the Periodic Table of Elements which appears on the inside cover of the CRC Handbook of Chemistry and Physics ('The Rubber Handbook'), 66th edition and using the CAS version notation.

The catalyst composition is preferably of the general formula:



The non-noble metal X is preferably one or two metals selected from iron, cobalt and nickel. Preferably X is selected from nickel, cobalt, and a combination of nickel and cobalt. Most preferably X represents nickel. The non-noble metal M may be selected from chromium, molybdenum and tungsten. Preferably M represents molybdenum.

The element represented by Z together with the oxygen component forms a refractory inorganic oxide. The element Z may be one or more elements selected from aluminium, silicon, magnesium, titanium, zirconium, boron, and zinc. Preferably Z represents one or more elements selected from aluminium, silicon, titanium and zinc. Most

preferably Z represents silicon as the predominant, especially the sole, element. Additional small amounts (in the range of from 1 to 3 wt%) of zinc oxide in the refractory material ZO can be advantageous to increase surface area of the catalyst compositions.

The numbers a, b, c, d and e represent relative molar ratio values which are estimated taking one component as a standard or reference. Herein one of b and c is to be taken as the reference and designated as the integer 1. The other values are then established as relative values, basis one of the metals X and M on an oxide basis.

Preferably c is the integer 1, and the ratio b:c is in the range of from 0.75:1 to 3:1, most preferably 0.8:1 to 2.5:1, especially 1:1; the ratio d:c is in the range 0.5:1 to 20:1, most preferably 0.75:1 to 10:1, especially 0.8:1 to 5:1; and the ratio e:c is in the range of from 1:1 to 50:1, most preferably 4:1 to 20:1, especially 5:1 to 10:1.

Depending on the method of preparation that is followed to prepare the catalyst composition for use in the invention, there could be residual ammonia, organic species and/or water species present; following different methods, different amounts as well as different types of species can be present. In respect of water, also atmospheric conditions can affect the amount present in the catalyst composition.

Therefore to ensure that the catalyst composition definition is not distorted by atmospheric or preparation conditions, the definition used herein, on both an elemental basis and on percentage amount basis, is given on an oxide basis.

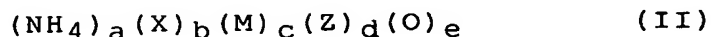
Preferably the amount of metal(s) X lies in the range of from 15 to 35 wt%, calculated as if the metal(s) are in their oxidic form and based on total catalyst weight, but more preferably is in the range of from 20 to 35 wt%,

and especially from 25 to 33 wt%. The metal M is suitably present in the highest amount of the two metal types; preferably the metal M is present in an amount in the range of from 40 to 75 wt% calculated as if the metal is in the oxidic form and based on total catalyst weight, more preferably 45 to 60 wt%, and especially 50 to 55 wt%. The balance of the catalyst, on an oxide basis, is comprised of a refractory oxide material, suitably in an amount in the range of from 5, preferably from 10, more preferably from 15, to 40 wt%, preferably to 30, more preferably to 25, especially to 20. Preferred compositions contain from 10 to 30 wt%, more preferably from 15 to 25 wt%, and especially substantially 20 wt%.

In a catalyst composition for use in the invention, there may be in the range of from 0 to 10 wt%, basis total catalyst, of residual species, eg organics, ammonia and/or water species, and most commonly from 5 to 8 wt%. The presence and amount of such components can be determined by standard analysis techniques.

Options and other preferences for the components of the bulk metal oxide catalysts of and for use in the invention are described below with reference to the general preparation technique.

The bulk metal oxide catalyst according to formula (I) is preferably prepared by decomposition of a precursor of the general formula



in which a is a number greater than 0, and X, M, Z, b, c, d and e have the meanings given above. The molar ratio of a:(b+c) is suitably from 0.1:1 to 5:1, preferably from 0.1:1 to 3:1, the molar ratio b:c is from 0.5:1 to 5:1, preferably from 0.75:1 to 3:1, especially 0.8:1 to 2.5:1. The molar ratio represented by d:c is suitably from 0.2:1 to 50:1, preferably from 0.5:1 to 20:1, more preferably

0.75:1 to 10:1, especially 0.8:1 to 5:1. The molar ratio represented by e:c is suitably from 1:1 to 50:1, more preferably 4:1 to 20:1, especially 5:1 to 10:1.

5 The decomposition of the precursor is performed at an elevated temperature in the range of from 100 to 600°C, preferably from 120 to 450°C, more preferably at a temperature in the range of from 250 to 350°C. The temperature most preferably is not in excess of around 350, especially 300°C, when amorphous material is wanted.
10 The decomposition may take place in an inert atmosphere, such as under nitrogen, any noble gas or a mixture thereof, or in an oxidative atmosphere, e.g. in oxygen, oxygen-nitrogen, air, or a mixture of one or more thereof, or in a reductive atmosphere, such as hydrogen,
15 hydrogen sulfide, or a mixture thereof. The decomposition may take place during processing of the slurry or during further processing of the composition for use, eg during extrusion or calcination before or after shaping.

The preparation of the precursor of general
20 formula II may be by the procedure described in for example EP-A-1 090 682, in which the metal compounds are fully dissolved in the liquid used, suitably a protic liquid, especially water. Most preferably preparation is by the process which involves contacting one or more
25 slurries of the desired metals in a protic liquid (for example water) wherein the metal compounds are in solid and dissolved phase simultaneously, with a refractory oxide in the presence of an alkali at a temperature and for a time sufficient to produce the precursor. Metal in
30 this context does not refer to the metals in metallic phase but to metallic compounds having the necessary metal ions in a less water-soluble form.

It is possible for all components to be added to the protic liquid at the same time or sequentially. Also it
35 is possible for one or more of the metal compounds and

the refractory oxide to be in slurry phase with the protic liquid, and for the remaining components to be added thereto.

5 The catalyst preparation process most suitably involves the mixing of slurry phase mixtures of the Group VIb and Group VIII metal(s) compounds in water or other protic liquid blended at elevated temperature with a slurry of an alkali and an inert oxide (preferably silica and/or alumina) also in water or other protic liquid. The
10 order of addition to form slurries from the individual compounds is not critical, but a slight benefit is seen when the alkali-refractory oxide slurry is added to the metals slurry.

15 Blending or mixing can be carried out for example with an Ultra Turrax machine.

During the mixing or blending process, the components of the slurries coprecipitate to form solids of the precursor composition under the action of the alkali precipitation agent. This process is suitably
20 controlled through the maintenance of an appropriate temperature for an appropriate time to achieve the desired precursor. It is a routine matter to determine the appropriate temperature/time combinations for a desired end product. Suitably the temperature will lie
25 in the range of from 25 to 95°C and the precipitation time will lie in the range of from 10 minutes to 2 hours. While essentially desired end products will arise from a control of both conditions, it is noted that operating the precipitation process at higher temperatures may
30 cause too much dissolution of the metals components to enable a good end-product; at too low a temperature then insufficient dissolution may occur.

In a preferred embodiment, an initial slurry concentration of in the range of from 2 to 40,
35 preferably 5 to 20 wt% of nominal solids content is aimed

for. By nominal solids content, the amount of solids added to the protic liquid is intended. Preferably the amount of alkali, eg ammonia, is at least 0.5 mol per mol of metals M+X, on an oxide basis, and at most 50 mol per mol of metals M+X, on an oxide basis. The quantity of alkaline material can affect the final form of the catalyst composition. Where the more active amorphous forms are desired, then the amount of alkaline material, eg ammonia, applied should be at least 0.75 mol, more preferably at least 0.8, especially at least 0.9 mol, per mol metals M+X, oxide basis. The alkali amount utilized is preferably at most 5 mol, more preferably at most 2 mol, and especially at most 1.7 mol per mol metals M+X, oxide basis.

The Group VIb metal is most preferably molybdenum. Suitable Group VIII metals include cobalt, nickel or a mixture thereof. Suitable nickel compounds, which stay in partly solid phase if the solvent is water, and therefore are preferred, are nickel carbonate, nickel oxide, nickel hydroxide, nickel phosphate, nickel formate, nickel sulfide, nickel molybdate, or a mixture of two or more thereof. Suitable, and preferred, molybdenum compounds (based on a similar criteria) are molybdenum (di or tri) oxide, ammonium molybdate, molybdic acid, molybdenum sulfide, or mixtures thereof. These materials are commercially available or can be prepared by commonly known laboratory practices, e.g. by precipitation.

Starting materials having a C, H, and O component in addition to the desired metals are, in general, more preferred due to a lesser impact on the environment. Nickel carbonate is therefore more preferred, since it can decompose to nickel oxide, carbon dioxide and water upon heating, based on the carbonate content of the starting material.

Suitable inert materials utilised in the refractory oxide component during preparation of the precursor are those which show less catalytic activity, or no catalytic activity at all in the utilisation of hydrogen under the conditions of use, compared to the metals utilised. The BET surface area of the inert materials suitably lies in the range of from 100 to 700 m²/g, more preferably from 150 to 400 m²/g. These materials include silica, alumina, magnesia, titania, zirconia, boria, zinc oxide, zinc hydroxide, natural and synthetic clays and mixtures of two or more thereof. Preferred materials are silica, alumina and titania, and mixtures thereof and/or with small amounts of zinc oxide. Most preferred is silica. The form of silica utilized is not limited and any silica commonly used in catalyst carriers may be utilized in the present invention. A very suitable silica material is Sipernat 50, a white silica powder having predominantly spherical particles, available from Degussa - Sipernat is a trade name.

Suitable alkalis applied to prepare the slurry with the inert material are selected from hydroxides or oxohydroxides, for example, Group IA or Group IIA hydroxides, Group IA or Group IIA silicates, Group IA or Group IIA carbonates, and equivalent ammonium compounds, or mixtures of any two or more thereof. Suitable examples include ammonium hydroxide, sodium hydroxide, ammonium silicate, ammonium carbonate, and sodium carbonate. Preferably the alkali compound is one that will generate ammonium ions in solution; this includes ammonia which with water as the solvent will generate the hydroxide form.

In one embodiment, a preferred starting material combination for the preparation of the bulk metal oxide precursor is nickel carbonate, molybdenum oxide and alumina. Other preferred combinations are nickel

carbonate, ammonium dimolybdate and silica, or nickel carbonate ammonium dimolybdate and titania.

It is generally preferred to utilise mixing and precipitation conditions, which keep the solvents below the boiling point temperatures of the applied solvent, i.e. below 100°C in case of water. The pH of the slurries is generally kept at their natural pH during the entire preparation process.

The formed slurry, where preferably all the metal components are present in solid and dissolved state simultaneously, is suitably held at ambient or elevated temperature for a period of time (commonly termed ageing) subsequent to the end of the precipitation process. The ageing time usually lies in the range of from 30 minutes to preferably 4 hours; the ageing temperature maybe in the range of from ambient temperature, for example, from 20, suitably from 25°C, to 95°C, preferably from 55 to 90, and especially from 60 to 80°C. The ageing period is optionally followed by cooling the obtained mixture to a lower temperature.

After optional cooling, the obtained slurry may be processed in a number of different ways in order to regain the solid content, which process can involve filtration, spray drying, flash drying, evaporation, and vacuum distillation. The system used will depend on a number of local factors including environmental legislations, and energy availability. Most preferred are filtration and spray drying. The former is quick and not energy intensive but requires several reiterative steps and produces higher volumes of waste water; the latter is energy intensive but generates little waste.

The preferred amorphous materials are more consistently obtained, at all refractory oxide contents, using the slurry preparation process of the invention.

The so-prepared solid product has a loss on ignition LOI of 5 to 95% and consists preferably of primarily amorphous material, as determined by means of powder X-ray diffraction analysis; however in some embodiments crystalline material, for example ammonium NiMo oxohydroxide with layered double hydroxide structure or a Co component may be present.

Herein loss on ignition (LOI) for a material is the relative amount of lost mass upon heating the material to 540°C following procedure: The sample is mixed well to prevent any inhomogeneity. The weighed sample is transferred into a weighed and precalcined crucible. The crucible is placed to a preheated oven at 540°C for a minimum time of 15 minutes, but typically for 1 hour. The crucible containing the dried sample is weighed again, and the LOI is determined according to the formula:

$$\text{LOI}\% = (w - w_{\text{calc}})/w * 100\%$$

where w is the original weight of the sample, w_{calc} is the weight of the calcined sample after heating in the oven, both corrected with the weight of the crucible.

The prepared powder may be dried before further processing, especially where filtration has been used to isolate the solids. This drying or ageing can take place in any suitable atmosphere, e.g. inert, such as nitrogen, noble gases, or mixtures thereof, or oxidative gases, such as oxygen, oxygen-nitrogen mixture, air, or mixtures thereof, or a reductive atmosphere, such as hydrogen, or mixtures of reductive and inert gases or mixtures thereof, with or without ammonia and/or water moisture present. The drying temperature is preferred to lie in the range of from 20, usually 25 to 95°C, preferably 55 to 90°C and especially from 70 to 80°C.

Optionally the obtained powder is calcined prior to shaping. Suitable calcination temperatures are in the range of from 100 to 600°C, preferably from 120 to 400°C.

Most preferably however calcination is not performed above 350°C, especially not above 300°C, in order to avoid formation of any crystalline material. The calcination may also be carried out in any suitable atmosphere, e.g. inert gases as nitrogen, noble gases or a mixture thereof, or in a reactive atmosphere, e.g. oxygen, oxygen-nitrogen, air, or a mixture of one or more thereof, or a mixture of inert and reactive gases.

Prior to shaping, the obtained powder is optionally mixed with additional materials in either solid or liquid phase. Those in solid state include catalytically active materials, e.g. other catalytic materials generally used in hydroprocessing applications.

Where desired, other supplementary materials can be added. These include materials usually added during conventional catalyst preparations. Suitable examples are phosphorus materials, e.g. phosphoric acid, ammonium phosphate, or organic phosphor compounds, boron compounds, fluor containing compounds, rare earth metals, additional transition metals, or mixtures thereof. Phosphorous compounds may be added at any step of the preparation. If e.g. alumina is used as binder, phosphorous compounds can be used for peptising (with or without nitric acid).

Moreover, added materials may include additives typically referred in the art as 'shaping agents' or 'shaping aids'. Those additives may comprise stearates, surfactants, graphite, or mixtures thereof. For maximum strength in the resulting shaped materials, particularly where shaping is by extrusion, then it is preferred to minimize the amount of any conventional extrusion aids.

Suitable materials in liquid phase may additionally be added to the shaping mixture obtained, which include protic, e.g. water, polyols, etc., and non-protic liquids, e.g. hydrocarbons. Protic liquids, e.g. water,

may be added for example in order to bring the LOI content of the mixture to a suitable level for shaping.

In general, there is no particular order of mixing the materials, in solid and/or liquid form, together.

5 What is important, is to ensure that the sample is mixed well to prevent nonhomogeneity. The amount of additional solids and liquids added during shaping lies preferentially in the range of from 0 to 95 wt% based on final weight, and depends on the requirements of the anticipated catalytic application. Shaping can be
10 performed in various ways depending on the requirements of the application. Those methods include spray drying, extrusion, beading and/or pelletizing among others.

Surface area of the final product measured by the
15 B.E.T. method, using nitrogen as adsorbate, generally lies in the range of from 10 to 350 m²/g, preferably above 35 m²/g, more preferably above 65 m²/g. Pore volume of the final product, measured using nitrogen adsorption up to 95nm on the B.E.T. adsorption curve, preferably
20 lies in the range of from 0.002 to 2.0 cm³/g, preferably from 0.1 to 1.0 cm³/g. Flat bed crush strength, as measured by ATSM D 6175, is preferably in excess of 50 N/cm, and lies more preferably above 100 N/cm, especially above 150 N/cm. The preferred amorphous
25 catalyst compositions of the present invention have been found to have such high crushing strengths.

The catalysts exhibit a very high activity for hydroprocessing of intermediate lubricating base oil products. This activity is higher than that found for
30 conventional NiMo and CoMo on alumina catalyst prepared by pore volume impregnation.

While not wishing to be bound to any theory, it is currently thought that this exceptional activity is the result of a high dispersion factor for the metals through
35 the oxide material, achieved through the careful control

of the precipitation process. The aim of the controlled precipitation process is to prevent the formation of as small as possible an amount of crystalline material. High dispersion should not be confused with uniformity of dispersion; the catalyst compositions for use in and of the invention have a high activity with metals dispersed through the oxide material, but not necessarily uniformly dispersed. Despite the amorphous nature of the preferred catalyst compositions, they still exhibit a high crushing strength. The preferred catalyst compositions used in the process of the present invention are substantially amorphous materials, which under powder X-ray diffraction (XRD) analysis have no detectable crystalline component. It remains within the scope of the process for some crystalline material, as detected by XRD, to be present in the catalyst; ideally it is present only in such an amount as to not change the activity of the amorphous material.

Since the base oil feed to be converted will contain sulphur-containing compounds, the catalyst used in the process is preferably at least partly sulphided prior to operation in order to increase its sulphur tolerance. Presulphiding of the catalyst can be achieved by methods known in the art, such as for instance those methods disclosed in the following publications EP-A-181254, EP-A-329499, EP-A-448435, EP-A-564317, WO-A-9302793 and WO-A-9425157.

In general, presulphiding is effected by contacting the unsulphided catalyst with a suitable sulphiding agent, such as hydrogen sulphide, elemental sulphur, a suitable polysulphide, a hydrocarbon oil containing a substantial amount of sulphur-containing compounds or a mixture of two or more of these sulphiding agents. Particularly for the in situ sulphidation a hydrocarbon oil containing a substantial amount of sulphur-containing

compounds may suitably be used as the sulphiding agent. Such oil is then contacted with the catalyst at a temperature which is gradually increased from ambient temperature to a temperature of between 150 and 250 °C.

5 The catalyst is to be maintained at this temperature for between 10 and 20 hours. Subsequently, the temperature is to be raised gradually to the operating temperature. A particular useful hydrocarbon oil presulphiding agent may be the base oil feed itself, which contains a significant
10 amount of sulphur-containing compounds. In this case the unsulphided catalyst may be contacted with the feed under, for example, the operating conditions, thus causing the catalyst to become sulphided. Typically, the base oil feed should comprise at least 0.5% by weight of
15 sulphur-containing compounds, said weight percentage indicating the amount of elemental sulphur relative to the total amount of feedstock, in order to be useful as a sulphiding agent.

The process according to the present invention is
20 operated at relatively mild conditions. The temperature is between 150 and 350 °C. The actual temperature will depend largely on the content of sulphur and/or nitrogen in the feed and the desired reduction to be achieved. Higher temperatures result in higher reduction of S- and
25 N-content. The pressure may range from 10 to 250 bar, but preferably is between 20 and 100 bar. The weight hourly space velocity (WHSV) may range from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l.h) and suitably is in the range from 0.2 to 5 kg/l.h.

30 The invention will be illustrated by the following non-limiting examples.

Example 1

Catalyst having the nominal composition of Ni-Mo-O/SiO₂ (26%-54%-20%).

109 g NiCO_3 (technical grade 39.5 wt%), 124 g ADM (ammonium dimolybdate technical grade 56.5 wt% Mo) and 45 g silica (Sipernat 50) was dispersed in 1485 g water at 80°C, while stirring, to form a slurry. 56 g ammonia solution (25 wt%) was mixed with the slurry, and aged for 1/2 hour. The warm mixture was pumped into a flask and the solids were recovered by means of spray drying, wherein the conditions were maintained such that the solids were not exposed to a temperature above 300°C. The obtained powder was pressed, crushed and sieved into 28/80 mesh size. Calcination was carried out at 300°C/1h, with a ramp of 200°C/hour from room temperature. Elemental structure of the catalyst as obtained:

$\text{Ni}_{1.1} \text{Mo}_{1.0} \text{Si}_{1.0} \text{O}_{6.1}$

The composition was seen to be amorphous by XRD analysis.

Comparative example A

A base oil obtained by performing an extraction with furfural on a vacuum distillate followed by a solvent dewaxing step using methylethylketone/toluene having the properties as listed in Table 1 was contacted with hydrogen and a commercial NiMo on alumina catalyst (C-424 of Criterion Catalyst Company, Houston, TX). The operating conditions were a hydrogen partial pressure of 100 bar, a WHSV of 1 kg/l/h, a recycle gas rate of 1000 Nl/kg and a temperature between 320°C and 360°C. The effluent was recovered and was distilled to give the base oil having a viscosity at 100°C greater than 4.7 cSt. The saturates content (wt%) and the VI of the base oils as obtained at various reaction temperatures are shown in respectively Figures 1 and 2. The properties of the end product recovered at a reaction temperature of 350°C are listed in Table 1.

Example 2

The comparative example was repeated, except in that the catalyst having the nominal composition of Ni-Mo-O/SiO₂ (26%-54%-20%), as prepared in Example 1, was used.

The properties of the end product, obtained at a reaction temperature of 350°C, are listed in Table 1. It is clearly shown in the figures 1 and 2 that the process using the Ni-Mo-O/SiO₂ bulk metal catalyst results in a higher amount of saturates and a higher VI at the same and even lower process temperatures.

TABLE 1

	Typical base oil feed-stock (*)	Compara tive example	Example 2
saturates (wt%) HPLC (SMS 2660)	73.3	92.3	98.5
Polars (Aromatics) (wt%)	26.7	7.7	1.5
sulphur (mg/kg)	7060		7
Nitrogen (mg/kg)	27		<1
Viscosity Index	104	112.5	119
viscosity at 100 °C (cSt)	5.23	5.027	4.907
viscosity at 40 °C (cSt)	30.09		25.24
pour point (°C)	-12	-10	-10

(*) as obtained by solvent extraction and solvent dewaxing

C L A I M S

1. Process to prepare a lubricating base oil having a saturate content of more than 90 wt%, a sulphur content of less than 0.03 wt% and a viscosity index of more than 80 starting from an intermediate lubricating base oil product having a saturates content of below 90 wt% and a sulphur content of above 0.03 wt%, which intermediate lubricating base oil product is obtained by first removing part of the aromatic compounds by means of solvent extraction of a petroleum fraction boiling in the lubricating base oil range resulting in a solvent extracted product and subsequently solvent dewaxing the solvent extracted product to obtain the intermediate lubricating base oil product wherein said intermediate product is contacted with a hydroprocessing catalyst in the presence of hydrogen, wherein said hydroprocessing catalyst comprises one or more metals of Group VIII and one or more metals of Group VIb in their oxide or sulfide form and the total content of the metals, calculated as if they are in their oxidic form, is greater than 60 wt%.

2. Process according to claim 1, wherein said hydroprocessing catalyst comprises one or more metals of Group VIII and one or more metals of Group VIb and a refractory oxide.

3. Process according to any one of claims 1-2, wherein the total content of the metals, calculated as if they are in their oxidic form, is greater than 75 wt%.

4. Process according to any one of claims 1-3, wherein the refractory oxide is 10 to 25 wt% as calculated in their oxide form.

6. Process according to claim 1, wherein the catalyst composition is of the general formula,

5

X represents at least one non-noble Group VIII metal;

Z represents one or more elements selected from

10

one of b and c is the integer 1;

15 d, e, and the other of b and c each are a number greater than 0 such that the molar ratio of b:c is in the range of from 0.5:1 to 5:1, the molar ratio of d:c is in the range of from 0.2:1 to 50:1, and the molar ratio of e:c is in the range of from 1.0 to 50.

20

8. Process according to any one of claims 1-7, wherein

30

10. Process according to any one of claims 1-9, wherein the viscosity index of the lubricating base oil is more than 120.

5 11. Process according to any one of claims 1-10, wherein the amount of saturates of the lubricating base oil is more than 96%.

A B S T R A C T

PROCESS TO PREPARE A BASE OIL

Process to prepare a lubricating base oil having a saturate content of more than 90 wt%, a sulphur content of less than 0.03 wt% and a viscosity index of more than 80 starting from an intermediate lubricating base oil product having a saturates content of below 90 wt% and a sulphur content of above 0.03 wt%, which intermediate lubricating base oil product is obtained by first removing part of the aromatic compounds by means of solvent extraction of a petroleum fraction boiling in the lubricating base oil range resulting in a solvent extracted product and subsequently solvent dewaxing the solvent extracted product to obtain the intermediate lubricating base oil product wherein said intermediate product is contacted with a hydroprocessing catalyst in the presence of hydrogen, wherein said hydroprocessing catalyst comprises one or more metals of Group VIII and one or more metals of Group VIb in their oxide or sulfide form and the total content of the metals, calculated as if they are in their oxidic form, is greater than 60 wt%.

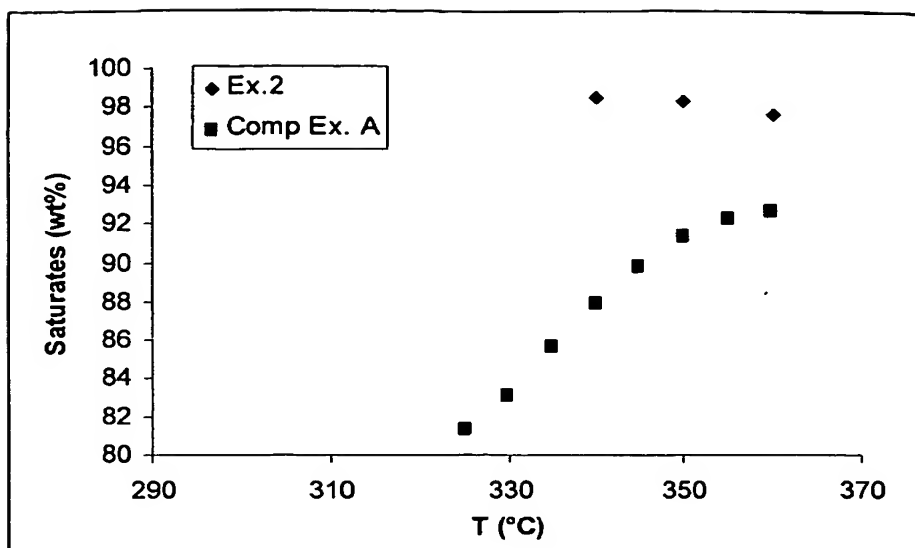


FIG 1

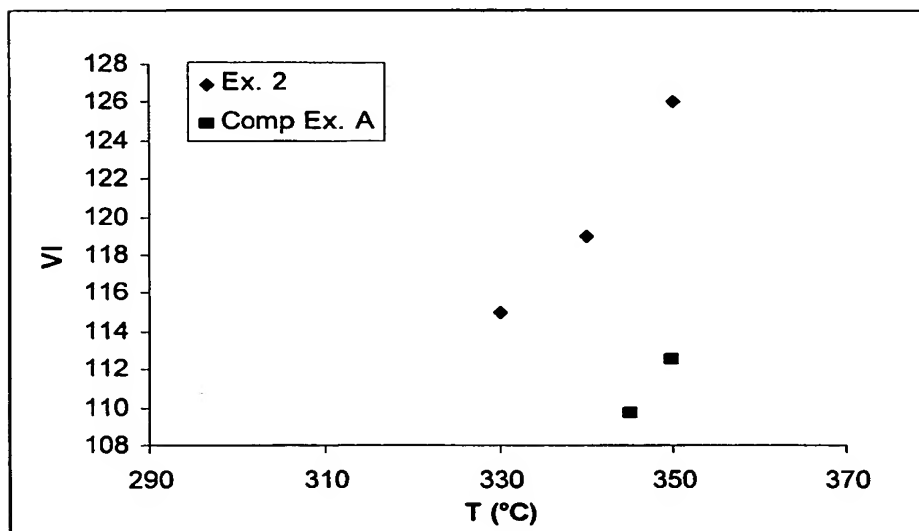


FIG 2

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

